California Department of Food and Agriculture Environmental Monitoring and Pest Management 1220 N Street, Room A-149 Sacramento, CA 95814

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BIOMONITORING INADVERTENT ORGANOPHOSPHATE PESTICIDE RESIDUES DURING SUMMER APPLICATIONS

I. INTRODUCTION

During the past two winters, the Environmental Hazards Assessment Program (EHAP) of the California Department of Food and Agriculture (CDFA) has conducted research on different organophosphate pesticides (OPs) used as dormant sprays in California orchards (Turner et al., 1989 and Turner et al., 1991). The investigations tried to determine the sources of inadvertent residues found on non-target row crops growing near these orchards. Results of the studies indicated that several organophosphate pesticides were transported to and deposited on non-target vegetation during fog and dry weather as a result of drift during application or post-application volatilization. In some instances, inadvertent residues of these pesticides were found on vegetable crops grown greater than a 1/4 mile from the pesticide application sites.

Results of a recent winter study indicated that dormant spray oil did not affect deposition of at least one OP, diazinon, on target and non-target crops either during or after application (Turner et al., 1991). It was originally hypothesized that dormant spray oil might increase pesticide deposition on target surfaces and reduce drift or volatilization of applied pesticides. If inadvertent OP residues occur on non-target crops during

winter months, perhaps some OPs applied during other times of the year (either with or without oil) also have the potential to move offsite onto non-target crops.

In order to examine whether this hypothesis is correct, the EHAP will undertake an investigation this summer to determine whether inadvertent residues of three OP's (diazinon, ethyl parathion, and chlorpyrifos) are likely to occur on non-target crops in three counties in the state.

II. OBJECTIVES

The objective is to determine if inadvertent residues of diazinon, ethyl parathion and chlorpyrifos occur on non-target crops as a result of application during summer months in California. Potted parsley and pepper plants will be used to biomonitor deposition and limited air sampling will measure ambient air concentrations of OPs.

III. PERSONNEL

This project will be under the supervision of Kean Goh. Primary project personnel are:

Russell Stein, Project Leader

Sally Powell, Experimental Design

Clarice Ando, Field Coordinator

Nancy Miller, Chemistry Lab Liaison

Jane Melvin, Chemist

Lisa Ross, Senior Scientist

Peter Stoddard, Public and Agency Liaison (916) 324-8916

IV. STUDY DESIGN

Organophosphate pesticides are used throughout the state in almost every month of the year. Three counties with high summer use of diazinon, chlorpyrifos and parathion were selected for inadvertent residue monitoring: Monterey, Fresno and Kern counties. The study area will be defined as that part of the county in which one or more of the OPs are applied during either June, July and/or August. Fourteen sites will be spaced equidistantly within the study area of each county. The area within a 1/4 mile radius surrounding a potential site will be surveyed to determine if commercial OP applications have taken place within 2 weeks of the beginning of the study. If no applications have occurred, the site will be considered acceptable. Private residences, city and county facilities, or commercial businesses will be the preferred site locations.

Biomonitoring of OP Deposition

Two vegetables, parsley and peppers, will be used as biomonitors for OP deposition. These choices were based on: 1) surface area and surface texture differences between species; 2) both are commercially grown in California and should be able to withstand the hot August temperatures of the Central Valley. Pots of each species will be placed at each site at the beginning of August and will remain there until the end of the month when they will be harvested and analyzed for total OP residues. A total of 14 samples per species per county will amount to 84 samples for the entire study.

Pesticide use reports for June, July and August from each county will be used to determine OP application date, amount, and location relative to our biomonitoring sites.

The average residue concentration contained in each species and its associated variability will be presented graphically along with pesticide use information for each county. It is possible that residue concentrations may vary significantly for different species since surface characteristics and canopy structure play an important role in gas-phase deposition (Sehmel, 1980).

If no residues are found on our samples within a county, we can state with 95% confidence that the true probability of collecting a sample containing inadvertent residues is less than 0.20 (20%) within that study area. In order to achieve this, our sample size (n) was determined as follows: The data from biomonitoring can be classified into two categories for each sample: detected or not detected. Random samples from such populations follow the bionomial distribution. If p is the probability of a "positive sample", n is the sample size, and x is the number of positive samples, using the binomial formula,

$$P(X=x) = {n \choose x} p^{X} (1-p)^{n-X} x=0,1,2,...,n,$$

and solving for n, the appropriate sample size was calculated to be 14 (Ross, 1984).

Ambient Air Concentrations

Ambient air concentrations will be measured using high volume air samplers at two sites within each county. Samples will be collected during two of the four weekly site visits made by the EHAP field crew for a total of 12 samples (2 sites x 2 days x 3 counties). Results will be used to corrobate biomonitoring deposition data.

V. SAMPLING METHODS

Biomonitoring

A vegetation sample will consist of 150 grams of leaf tissue. One sample of each species will be collected and the number of exposure days will be recorded at the end of the month at each site. Samples will be kept in large mouth 1-liter jars on wet ice or in refrigerators until analysis. Site visits will be made at weekly intervals to interview owners about local commercial pesticide applications and to irrigate sample material.

Air Sampling

An air sample will consist of 125-ml pre-washed XAD-2 resin. The high volume air sampling rate will be precalibrated at 1000 l/min. Any detectable concentration will be calculated as a time-weighted average ambient air concentration collected during an 8-hour period. Air samplers will undergo post-sample calibration checks to ensure correct sampling flowrates. Resin samples will be frozen on dry ice or placed in freezers until analysis.

Chain of custody records will document sample handling throughout the study period.

VI. CHEMISTRY METHODS

Residues of diazinon, ethyl parathion, chlorpyrifos and their oxidation products will be extracted from vegetation samples using acetonitrile and from air samples using acetone. Analysis will be performed by gas chromatography using a flame photometric detector.

Results will be reported in micrograms per sample for both vegetation and air samples. Results will be reported in both wet and dry weights for vegetation samples.

VII. QUALITY CONTROL

Biomonitoring Samples

Background samples will be collected from flats of each species to determine possible OP residue levels prior to beginning the study. During the study, vegetation samples will be split for quality control analysis between CDFA and the quality control laboratory. A total of 12 samples will be analyzed by the quality control lab: 2 species x 2 sites x 3 counties. For continuous quality control during analysis, one blank matrix and blank matrix spike will be analyzed with each extraction set. Results will be presented in the report appendix.

Air Samples

One blank matrix and blank matrix spike will be analyzed with each extraction set. Air samples cannot be split for quality control analysis.

VIII. TIMETABLE

The vegetation will be set out at all sites by August 1 and sample collection will take place during the final days of the month. Chemical analysis should be completed by September 30, 1991. A rough draft of the report will be ready for review by November 30, with final review and approval expected by January 31, 1992.

IX. REFERENCES

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Turner, B., S. Powell, N. Miller and J. Melvin, 1989. A field study of fog and dry deposition as sources of inadvertent pesticide residues on row crops. Ca. Dept. Food and Agric. Report EH 89-11.

Turner, B., S. Powell, D. Gonzalez and C. Ando, 1991. The influence of dormant spray oil on diazinon deposition and transfer to non-target vegetation. Ca. Dept. Food and Agric. Report EH 91-2.

Sehmel, G. A., 1980. Particle and gas dry deposition: A review. Atmospheric Environment 14:983-1011.

Ross, S., 1984. A first course in probability. 2nd Ed., Macmillan Publishing Company, New York, p. 119.

X. BUDGET

Personnel Costs

ERS, 6 mo @ half-time \$ 9000 Assoc. ERS, 6 mo @ half-time 12000

Operating Expenses

Per Diem:

60 days @ \$84 ea: 5040 Matl/Eqpmt: 1000

Chemistry:

108 samples @ \$200 ea: 21600

TOTAL ESTIMATED COST: \$48640